

Comment on "Curvature capillary migration of microspheres" by N. Sharifi-Mood, I.B. Liu, K.J. Stebe, *Soft Matter*, 2015, 11, 6768, arXiv:1502.01672

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In a recent paper, Sharifi-Mood et al. study colloidal particles trapped at a liquid interface with opposite principal curvatures $c_1 = -c_2$. In the theory part, they claim that the trapping energy vanishes at second order in $\Delta c = c_1 - c_2$, which would invalidate our previous result [Phys. Rev. E, 2006, 74, 041402]. Here we show that this claim arises from an improper treatment of the outer boundary condition on the deformation field. For both pinned and moving contact lines, we find that the outer boundary is irrelevant, which confirms our previous work. More generally, we show that the trapping energy is determined by the deformation close to the particle and does not depend on the far-field.

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Colloidal particles trapped at a curved liquid interface are subject to capillary forces that do not depend on their mass or charge but on geometrical parameters only. In Ref. [1], Sharifi-Mood et al. provide an interesting analysis of the role of contact line pinning. Regarding the trapping energy, however, these authors assert that it vanishes at second order, contrary to previous work, and they state that "the origin of the discrepancy is an inappropriate treatment of the contour integral" in [2]. The present comment intends to refute this claim of [1], to unambiguously determine the trapping energy, and to clarify the role of the far-field.

Previous works [2–4] rely on the assumption that curvature-induced forces arise from the interface close to the particle and that the far-field is irrelevant. Thus the profile of the bare interface is taken in small-gradient approximation, $h_0 = \frac{\Delta c}{4} \cos(2\varphi) r^2$, which is valid only at distances shorter than the curvature radius $R_c = 1/\Delta c$. Adding a particle modifies the profile as $h = h_0 + \eta$, where the deformation field

$$\eta = \frac{\Delta c}{12} \cos 2\varphi \frac{r_0^4}{r^2}. \quad (1)$$

is determined from the contact angle at the particle surface. By the same token, the trapping energy comprises only near-field contributions, and is given by the boundary term along the contact line of radius r_0 ,

$$E_{\text{in}} = \gamma \oint_{r_0} \eta \nabla h_0 \cdot \mathbf{n} ds = -\frac{\pi}{24} \gamma r_0^4 \Delta c^2. \quad (2)$$

Since a similar line integral of $\eta \nabla \eta$ is cancelled by the area change due to displacement of the contact line on the particle surface, one obtains the curvature-dependent energy $E = E_{\text{in}}$ [2], which was confirmed in [3, 4].

Sharifi-Mood et al. attempt to go beyond the near-field approach and to evaluate the term arising at the outer boundary,

$$E_{\text{out}} = \gamma \oint_{R_{\text{out}}} \eta \nabla h_0 \cdot \mathbf{n} ds, \quad (3)$$

where, in the simplest geometry, $R_{\text{out}}(\varphi)$ is the distance of the container wall from the particle. Using the above

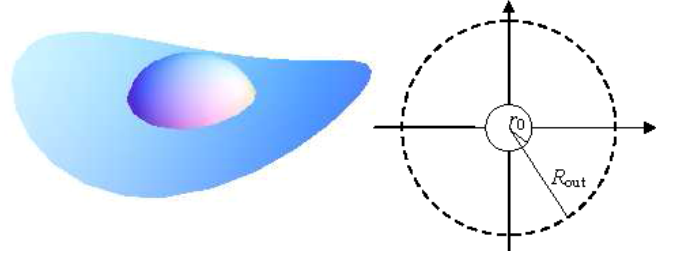


FIG. 1: Schematic view of a particle trapped at a liquid interface with zero mean curvature, $c_1 + c_2 = 0$. The right panel shows the simple case of a circular interface of radius R_{out} (dashed line); the inner circle indicates the contact line of radius r_0 on the particle.

expressions $h_0 \propto r^2$ and $\eta \propto r^{-2}$, and letting $R_{\text{out}} \rightarrow \infty$, these authors find in (24) of [1] the relation $E_{\text{out}} = -E_{\text{in}}$. This leads them to the conclusion that the trapping energy vanishes at second order, $E = E_{\text{in}} + E_{\text{out}} = O(\Delta c^4)$.

Yet this argument is flawed by the fact that E_{out} is calculated with the near-field deformation (1) which is not correct at R_{out} . (Moreover, $h_0 \propto r^2$ is valid at distances within the curvature radius only [5].) In the following we evaluate E_{out} with the correct deformation field η , which satisfies appropriate conditions at the outer boundary. For both pinned and moving contact lines, we find that the outer boundary does not contribute to E , and thus confirm the results from the near-field approach and in particular the trapping energy $E = E_{\text{in}}$ of [2].

Pinned outer contact line

In many experiments, the outer boundary pins the interface at a fixed contact line, $h_0|_{R_{\text{out}}} = K(\varphi)$; examples are the micropost in Fig. 5 of [1] or pinning due to the surface roughness of the container wall. The same contact line delimits the deformed profile, $h|_{R_{\text{out}}} = K(\varphi)$, which implies

$$\eta|_{R_{\text{out}}} = (h - h_0)|_{R_{\text{out}}} = 0. \quad (4)$$

As a consequence, the contour integral in (3) vanishes, and the trapping energy is $E = E_{\text{in}}$.

As a simple example, we consider a particle at the center of a circular interface with constant R_{out} , as in Fig. 1. One readily finds the form

$$\eta = \frac{\Delta c}{12} \cos 2\varphi \left(\frac{r_0^4}{r^2} - \frac{r_0^4 r^2}{R_{\text{out}}^4} \right) \xi, \quad (5)$$

which solves Laplace's equation $\nabla^2 \eta = 0$ and satisfies (4) and thus $E_{\text{out}} = 0$. (The factor $\xi = 1/(1 + r_0^4/R_{\text{out}}^4) \approx 1$ assures the boundary condition on the particle surface.)

Moving contact line

Though the preceding paragraphs refute the claim of [1], we complete the discussion by considering the case where the contact line at the outer boundary is not pinned but moves on the confining walls. Then the boundary condition involves the gradient of the profile, $L(\varphi) = \mathbf{n} \cdot \nabla h_0|_{R_{\text{out}}}$. The same condition applies to the deformed interface $h = h_0 + \eta$, implying

$$\mathbf{n} \cdot \nabla \eta|_{R_{\text{out}}} = \mathbf{n} \cdot \nabla (h - h_0)|_{R_{\text{out}}} = 0. \quad (6)$$

It is straightforward to show that the corresponding boundary term E_{out} does not vanish, yet is cancelled by the area change E_A due to the moving contact line, resulting in $E = E_{\text{in}}$. (In previous work, the area change has been considered at the inner boundary only; cf. E_P in [2] or Eq. (26) in [1].) For the circular interface of Fig. 1, the deformation field is similar to (5), albeit with a plus sign instead of the minus; one readily calculates the integrated term at the outer boundary $E_{\text{out}} = -2E_{\text{in}}$, and the area change $E_A = 2E_{\text{in}}$. Since these terms cancel each other, one has $E = E_{\text{in}}$.

In summary, when properly treating the outer boundary condition, for both pinned and moving contact lines, we find as a rather general result that the outer boundary does not contribute to the trapping energy. This invalidates the claim $E = O(\Delta c^4)$ of [1], supports the near-field approach of [2], and confirms the trapping energy $E = E_{\text{in}}$ obtained previously. Retaining this quadratic term would modify the analysis of the experimental results of [1], for example the fits in Fig. 7, yet does not affect the qualitative interpretation in terms of contact line pinning.

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